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(54) Process for dewaxing hydrocarbon feedstocks

(57) A process for eliminating waxy paraffins from hydrocarbon feedstocks having a boiling temperature of from about 180°C to about 650°C and containing sulphur, by selective cracking of the straight chain paraffinic hydrocarbons, consisting in passing said feedstock over a crystalline silica polymorph of the silicalite type under suitable operating conditions for cracking the straight chain paraffins.

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SPECIFICATION

Process for Dewaxing Hydrocarbon Feedstocks

The present invention relates to a process for removing waxy paraffins from hydrocarbon feedstocks at temperatures ranging from 180°C to 650°C (i.e. in the gasoil range). The process of the invention also concerns a process for decreasing the cloud point of those hydrocarbon feedstocks. Particularly the invention relates to processes which are tolerant to sulphur containing feedstocks.

In order to produce gasoils or lubricating oils, it often happens that waxy paraffinic hydrocarbons have to be removed from the liquid hydrocarbon feedstocks. More particularly in the production of gasoils, the removal of these waxy hydrocarbons is necessary because their presence leads to too high cloud points, resulting in a reduction of the efficiency of these gasoils at low temperatures.

Processes for removing these waxy paraffins are known in the art. Generally those processes consist of a treatment with a suitable solvent, but catalytic processes are also known to remove these paraffins.

U.S. Patent 3,700,585 discloses a process for removing the waxy paraffins from hydrocarbon feedstocks in the presence of zeolites. These zeolites are crystalline aluminosilicates which have an ion exchange capacity. In this patent the use of a ZSM-5, under its hydrogenated form or not, is specifically described, together with a ZSM-8 zeolite. Moreover the treated feedstocks have a very low sulphur content.

European Patent 82,019 also discloses a process to selectively remove the waxy paraffinic hydrocarbons, by passing the hydrocarbon feed over a zeolite modified with an organic silane compound, and in the presence of hydrogen. Moreover the treated feedstocks have also a very low sulphur content.

According to U.S. Patent 4,428,825, it is taught that the reaction is carried out in the presence of an hydrogenation catalyst or still in the presence of a zeolite or a silicalite impregnated with a catalytic metal, and in the presence of ammonia or of an ammonia precursor.

Moreover, although all these catalysts are impregnated with catalytically active metals, the silicalite or the zeolite being used as a carrier only, the reduction of the pour point or the cloud point is not sufficient in order to use efficiently the gasoils at low temperatures. Moreover the sulphur content of the feed is extremely low.

There is therefore a need for a process which enables to remove the waxy paraffins in such way that the resulting gasoils can be efficiently used at low temperatures.

The object of the present invention is to provide an improved process for removing the waxy paraffins from hydrocarbon feedstocks boiling in the range comprised between about 180°C and about 650°C, and having a sulphur content of about 1% by weight or more.

Another object of the present invention is to provide a process for removing the waxy paraffins from gasoils feedstocks including light gasoils, heavy gasoils, vacuum gasoils, atmospheric gasoils and deasphalted oils.

Another object of the present invention is to provide a process for removing the waxy paraffins from gasoils feedstocks, which enables not to reduce too much the cetane index of the gasoil.

The process of the present invention for removing the waxy paraffins from hydrocarbon feedstocks boiling at temperatures ranging from 180°C to 650°C and containing sulphur by selective cracking of the straight chain paraffinic hydrocarbons consists in passing said hydrocarbon feedstock over a crystalline silica polymorph of the silicalite type under suitable operating conditions for cracking the straight chain paraffins.

The Applicant has now unexpectedly found that by passing an hydrocarbon feedstock boiling at temperatures ranging from 180°C to 650°C, particularly in the gasoil boiling range and containing sulphur in an amount heretofore considered to be unacceptable to zeolite catalysts, over a crystalline silica polymorph of the silicalite type as catalyst, under operating conditions suitable for the cracking of paraffins, a gasoil is obtained with a reduced content in paraffinic hydrocarbons, and said gasoil having not only a lower pour point than that generally obtained in accordance with prior processes, but having in addition a cetane index practically identical to that of the feed.

The cetane index is a very important factor to be considered in the gasoils; indeed, if the cetane index goes down below a value of about 35, problems of starting of engines using such gasoils are encountered; this drawback may be overcome by adding various additives which make the starting of the engine easy. It is therefore of particular importance to maintain the cetane index at a value of from 40 to 50.

The catalyst used in the process of the invention is a crystalline silica polymorph of the silicalite type. These silicalites, by contrast with aluminosilicates of the zeolite type which are silicates of aluminium and sodium and/or calcium, have no ion exchange capacity since the AlO_4^- tetrahedra are not part of the crystalline network. However, aluminium may be present in silicalite, but in the form of impurity which comes from the silica source used to prepare silicalite. It may be said that silicalites which contain this type of aluminium or other metal oxides as impurity, may not be considered as metallosilicates.

The description together with the methods for preparing the silicalites are given in U.S. Patent 4,061,724 which is incorporated herein by reference.

An important distinction which is employed to advantage in the present invention, lies in the tolerance of the silicalite catalyst to sulphur concentrations heretofore thought to be unacceptable at the conversion conditions employed in the dewaxing of gasoils. As noted previously, the teaching of prior processes for the dewaxing over zeolite catalysts is very strict, permitting no more than about 0.2% by weight sulphur.

These conditions generally necessitate to desulfurize the feedstock before submitting it to a dewaxing process.

In contrast to the low sulphur tolerance of the zeolite catalysts heretofore employed in the dewaxing of hydrocarbons feedstocks, the silicalite catalyst employed in the present invention permits the use of gasoils feedstocks having sulphur contamination levels much higher than those heretofore considered to be acceptable since feedstocks having up to 5% sulphur may be treated. This offers an important commercial advantage since it increases the availability of hydrocarbon feedstocks for the conversion process. Experimental work described in greater detail hereinafter indicates that a sulphur contamination up to about 5% is readily tolerated and a preferred application of the invention is in the dewaxing of deasphalted oil or light gasoils containing sulphur in an amount greater than about 1% by weight.

A further advantage of the present invention resides in the fact that a steam cofeed may be employed, not withstanding that the feed stream to the reaction zone contains sulphur in amounts above what has been heretofore considered to be acceptable. In fact, it is believed that an effective amount of steam in the cofeed actually reduces coking due to sulphur and therefore increases the useful life of the catalyst.

The process of the invention for removing the waxy paraffins from hydrocarbon feedstocks boiling at temperatures ranging from 180°C to 650°C, including the various types of gasoils, may be carried out in any suitable apparatus, which comprises a reaction zone which contains the silicalite catalyst. The silicalite catalyst may be introduced in the reaction zone either in the form of a single bed or in the form of a multiple bed. On both sides of the catalytic beds, layers of inert materials are generally introduced.

A preferred catalyst for use in the dewaxing of the hydrocarbon feedstocks boiling at temperatures from 180°C to 650°C in accordance with the present invention is a silicalite having a crystallite size of less than 8 microns and a ratio of silica to alumina in the tetrahedral molecular network of at least 200.

Among the gasoil feeds which may be treated in accordance with the process of the invention, the light gasoils may be used. The light gasoils have boiling points of from 180°C to 320°C. They are obtained by atmospheric distillation. Another straight-run cut also obtained by atmospheric distillation may also be treated. These cuts give the heavy gasoils, which have a boiling point of from 320°C to 375°C. Besides the cuts of the atmospheric distillation, it is possible also to treat the vacuum gasoils which result from fractions obtained by vacuum distillation. These vacuum gasoils have boiling points of from 370°C to 530°C.

In addition, deasphalted oil may also be dewaxed with the process of the invention. The deasphalted oils are obtained by butane extraction of the 530°C residue.

In accordance with the process of the invention, the feed is passed in the reaction zone containing the silicalite catalyst at a temperature of from 350°C to 450°C and preferably from 380°C to 420°C. The feed is passed under a pressure of from atmospheric pressure to 80 bars, and preferably from 35 to 60 bars, and at a hourly space velocity of from 0.1 to 20, preferably from 0.5 to 5. Simultaneously with the feed, hydrogen is introduced into the reaction zone in such an amount that the H_2/HC ratio is from 50 to 5000 NL/L and preferably from 50 to 500 NL/L (the hydrogen volume being measured in the gaseous state and under standard conditions). Practically however, only a small fraction of the hydrogen reacts, and the gas recovered at the reactor outlet, comprising hydrogen and a small amount of gaseous hydrocarbons, is generally recycled. To compensate for the hydrogen consumption, a fraction of the recycled gas is continuously replaced by fresh hydrogen.

The following examples are given in order to better illustrate the process of the invention, but without limiting its scope.

EXAMPLE 1

A feed containing light gasoil having the characteristics indicated in Table 1, was treated.

TABLE 1

$d_{15/4}$	0.852
Distillation: wt%	IBP—180°C: 2.5 180—350°C: 94.5 350^{+}°C: 3.0
n-paraffin content	43% by wt
Sulphur	0.903% by wt
Pour point	−3°C
Viscosity at 50°C (sSt)	2.9
Cetane index	50

The feed was passed into a reactor which contained a bed of silicalite catalyst disposed between two

layers of inert materials. Simultaneously, hydrogen was introduced into the reactor. The hydrogen was used in an amount such that the H_2/HC ratio was 360 NL/L.

The feed was passed at different temperatures, pressures and LHSV, which are indicated in Table 2. The obtained results are also indicated in Table 2.

TABLE 2

	LHSV 0.8			LHSV 1		
Temperature (°C)	380	400	420	380	400	420
Sulphur (wt %)	1.118	1.030	0.949	1.095	1.040	0.964
n-paraffin (% by wt)	13	19	26	14	19	22
Cloud point (°C)		<−51°C			<−51°C	
Pour point (°C)		<−51°C			<−51°C	
Viscosity at 50°C (cSt)	3.23	3.22	3.14	3.30	3.13	3.14
Specific gravity (d 15/4)	0.880	0.879	0.880	0.877	0.878	0.879
Cetane index	43	43	43	44	43	43

EXAMPLE 2

A feed which contained light gasoils and having the cahracteristics indicated in Table 3, was treated.

TABLE 3
Feed Properties

Specific gravity ($d_{15/4}$)	0.852
Cetane index	50.2
Cloud point	−5°C
Pour point	−9°C
% volume distilled at 350°C	97%
n-paraffin content	34%
Sulphur content	0.9%

The feed was passed into a reactor which contained a bed of silicalite catalyst disposed between two layers of an inert material. The operating conditions were as follows:

Temperature	360°C
LHSV	4
H_2/HC	360 NL/L
Pressure	40 Bars

The obtained results are indicated in Table 4.

TABLE 4

Distillation (wt %)	
Gas	0.2
C_3+C_4	9.3
C_5–180°C	11.7
180°C+	78.8
Properties of the 180±°C	
$d_{15/4}$	0.863
Distillation vol % at 250°C	10%
350°C	>90%
Pour point	−39°C
Cloud point	−32°C
Cetane index	46.1

Properties of the C_5–180°C
The Percentages specified were determined by gas chromatography using a capillary column.

PONA (Paraffins	25%
Olefins	56%
Naphthenes	7%
Aromatics)	5%
Unidentified by gas chromatography	7%
RON	86
MON	74.8

EXAMPLE 3

A feed containing a heavy gasoil, which resulted from atmospheric distillation, was treated. The heavy gasoil has a boiling point generally from 320°C to 375°C. The characteristics of the heavy gasoil are indicated in Table 5.

TABLE 5
Properties of the Feed

$d_{15/4}$	0.882
Distillation IBP–180°C	0.6% by wt
180–350°C	32.1% by wt
350°C+	67.3% by wt
n-paraffins	25.4%
Sulphur content	0.9% by wt

Fraction	180°C–350°C	350°C±
Pour point	−12°C	24°C
Cloud point	−9°C	—
Cetane index	48.8	46.9

This feed was passed in a reactor containing a bed of silicalite catalyst disposed between two layers of inert material.

The operating conditions were as follows:

Pressure	35 bars
H_2/HC	300 NL/L
LHSV	2, 4, 6

The obtained results are indicated in Table 6.

TABLE 6

Temperature (°C)	350			380			Feed
LHSV	2 H	4 B	6 C	2 G	4 F	6 E	
Properties of the 180—350°C fraction							
$d_{15/4}$	0.876		0.866	0.881	0.879	0.871	0.863
Pour point (°C)	−21	—	−9	<−50	−36	−21	−9
Cloud point (°C)	−17	—	−11	<−50	−28	−19	−12
Cetane index	46.3	—	48.8	44.8	46	47.5	48.8
Properties of the 350^{+}°C fraction							
$d_{15/4}$	0.906	0.908	0.893	0.921	0.914	0.902	0.893
Pour point (°C)	12	0	18.3	−33	−6	9	24
Cloud point (°C)	13	+6	21.1	—	2	11	—
Cetane index	45	44	47	40	43	45.5	46.9
Total liquid effluent properties n-Paraffin (% by wt)	14.8	11.8	19.9	6.8	12.6	15.0	25.4

EXAMPLE 4

A feed constituted of a vacuum gasoil was treated. The vacuum gasoils generally have a boiling point ranging from 370°C to 530°C, and are obtained by vacuum distillation. The properties of the feed are indicated in Table 7.

TABLE 7

Average feed properties

Boiling point range (°C)	IBP—180	180—250	250—370	370—500	500+	Total feed
Yield (% w)	0.1	2.55	18.39	64.55	14.41	100
$d_{15/4}$	—	0.831	0.886	0.9179		0.91
S (% w)	0.05	0.646	1.330	1.435	1.680	1.42
				(1.476)		
N total (ppm)	—	16	200	1.220		1010
N basic (ppm)	—	6	65	321		267
Carbon Conradson (% w)				0.42		
Viscosity at 100°C				7.62		
„ „ 120°C (cStokes)				4.87		
Refractive index				1.488		
Aniline point (°C)				86.6		
Bromine number						4
Cetane index			44.8			
Pour point (°C)			0			
Cloud point (°C)			−2			

This feed was passed into a reactor containing a bed of silicalite catalyst disposed between two layers of inert material. The operating conditions were as follows:

Pressure:	54 bars
Temperature:	405°C
LHSV:	3

The dewaxed feed had the following composition and properties:

Composition

Fuel gas	1%
C_3+C_4	2.0%
C_5—180°C	3.2%
180°C—250°C	2.3%
250°C—370°C	17.8%
370^{+}°C	73.7%

Properties Fraction	$d_{15/4}$	Aniline point	Pour point	Cloud point	Refract. index (80°C)
180°C—250°C	0.838	—	—	—	—
250°C—370°C	0.903	54.4°C	−27°C	−24°C	—
370^{+}°C	0.93	87.2°C	—	—	1.496

This table shows a reduction of the pour point and cloud point, together with a reduction of the aniline point, and an increase of the refractive index. All these variations indicate a significant reduction of the n-paraffin content of the feed.

EXAMPLE 5

A feed constituted of a deasphalted oil was treated. Deasphalted oil is obtained by butane extraction of the vacuum distillation residue at 530°C. The properties of the feed are indicated in Table 8.

TABLE 8

Density $d_{15/4}$	0.9245
Distillation:	
IBP—370°C	2%
370°C^{+}	98%
Sulphur	3.64%
Total nitrogen	560 ppm
Basic nitrogen	170 ppm
Carbon Conradson	1.37 wt%
Viscosity	
at 100°C	18.88 cSt
at 120°C	9.76 cSt
Aniline point	
350—540°C	87°C
540°C^{+}	106°C
Pour point	higher than 43°C

This feed was passed into a reactor containing a bed of silicalite catalyst disposed between two layers of inert material. The operating conditions were as follows:

Pressure:	60 bars
Temperature:	390°C
LHSV:	1
H_2/HC volume ratio:	100 NL/L

The dewaxed feed had the following composition and properties:

Composition (wt%)		
	C_1—C_2	1.03
	C_3	4.37
	C_4	2.72
	IBP—180°C	4.29
	180—350°C	3.15
	350—540°C	51.23
	540°C$^+$	33.21
Properties of the 350—540°C fraction		
	Viscosity index	60
	Pour point	6°C
	Aniline point	83.2°C
Properties of the 540°C± fraction		
	Viscosity index	75
	Pour point	6°C
	Carbon Conradson	4.33 wt%

These results show a reduction of the aniline point and a considerable reduction of the pour point, both showing a significant reduction of the n-paraffin content of the feed.

Moreover, it is worth noting that the sulphur content of the feed is high, and that some fractions of said feed had a sulphur content of 4.1 wt%. Even at such high values of sulphur content has no catalyst deactivation been observed.

CLAIMS

1. A process for removing waxy paraffins from hydrocarbon feedstocks boiling at temperatures ranging from 180°C to 650°C and containing sulphur by selective cracking of straight chain paraffinic hydrocarbons, which process comprises passing said hydrocarbon feedstock over a crystalline silica polymorph of the silicalite type under suitable operating conditions for cracking the straight chain paraffins.

2. A process according to Claim 1, wherein said feedstock contains sulphur in an amount of at least about 1% by weight.

3. A process according to Claim 1 or Claim 2, wherein said feedstock contains sulphur in an amount of from 1 to 5% by weight.

4. A process according to any one of Claims 1 to 3 wherein the hydrocarbon feedstock is a light gasoil which boils at a temperature of from 180°C to 320°C.

5. A process according to any one of Claims 1 to 3 wherein the hydrocarbon feedstock is a heavy gasoil which boils at a temperature of from 320°C to 375°C.

6. A process according to any one of Claims 1 to 3 wherein the hydrocarbon feedstock is a vacuum gasoil which boils at a temperature of from 370°C to 530°C.

7. A process according to any one of Claims 1 to 3 wherein the hydrocarbon feedstock is a deasphalted oil.

8. A process according to any foregoing claim wherein the hydrocarbon feedstock is passed over a crystalline silica polymorph of the silicalite type at a temperature of from 350°C to 450°C, at a pressure of from atmospheric pressure to 80 bars, and at a liquid hourly space velocity of from 0.1 to 20.

9. A process according to Claim 8 wherein the hydrocarbon feedstock is passed over the crystalline silica polymorph of the silicalite type at a temperature of from 380°C to 420°C.

10. A process according to Claim 8 or Claim 9 wherein the hydrocarbon feedstock is passed over the crystalline silica polymorph of the silicalite type at a pressure of from 35 to 60 bars.

11. A process according to any one of Claims 8 to 10 wherein the hydrocarbon feedstock is passed over the crystalline silica polymorph of the silicalite type at a LHSV of from 0.5 to 5.

12. A process according to any one of Claims 8 to 11 wherein the hydrocarbon feedstock is passed over the crystalline silica polymorph of the silicalite type simultaneously with an hydrogen stream used in an amount such that H_2/HC ratio is from 50 to 50000 NL/L.

13. A process according to Claim 12 wherein the H_2/HC ratio is from 50 to 500 NL/L.

14. A process for removing waxy paraffins from hydrocarbon feedstocks substantially as hereinbefore described in any of the foregoing Examples.

15. Hydrocarbon feedstocks whenever treated by the process of any foregoing claim.

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